

CLAIMS

1. A method of lowering MFR response of a high-melt-flow-rate-polymer-producing metallocene catalyst comprising contacting the metallocene catalyst with a sufficient quantity of α,ω -diene monomer such that when the catalyst composition is contacted with polymerizable reactants under suitable polymerization conditions, the resulting polymer has
an MFR in the range of 0.1 to 19 g/10min.
2. The method of claim 1 wherein the α,ω -diene is present in the range of 10 to 20,000 ppm of the polymerizable reactants.
3. The method of claim 1 wherein the metallocene catalyst is further defined as a zirconium metallocene catalyst.
4. The method of claim 1 wherein the polymerizable reactants are propylene monomers.
5. The method of claim 1 wherein the polymerization conditions are further defined as slurry polymerization conditions.
6. The method of claim 1 wherein the polymerization conditions further includes the presence of hydrogen.
7. A method of lowering MFR response of a high-melt-flow-rate-polymer-producing metallocene catalyst in the presence of hydrogen in the range of 100 to 50,000 ppm comprising contacting the metallocene catalyst with a sufficient quantity of α,ω -diene monomer such that when the catalyst composition is contacted with propylene monomers under suitable polymerization conditions, the resulting polymer has
an MFR in the range of 0.1 to 19 g/10min.

8. The method of claim 7 wherein the metallocene catalyst is further defined as a zirconium metallocene catalyst.
9. The method of claim 7 wherein the α,ω -diene is present in the range of 10 to 20,000 ppm of the propylene monomers.
10. The method of claim 7 wherein the α,ω -diene monomer is 1,9-decadiene.
11. A method of lowering MFR response of a high-melt-flow-rate-polymer-producing zirconium metallocene catalyst in the presence of ethylene monomers comprising contacting the zirconium metallocene catalyst with a sufficient quantity of α,ω -diene monomer such that when the catalyst composition is contacted with propylene monomers under suitable polymerization conditions the resulting polymer has
 - an MFR in the range of 0.1 to 19 g/10min.
12. The method of claim 11 wherein the α,ω -diene is present in the range of 10 to 20,000 ppm.
13. The method of claim 11 wherein the α,ω -diene monomer is 1,9-decadiene.
14. A method of forming a propylene polymer having a MFR in the range of 0.1 to 19 comprising:
contacting a high melt flow rate polymer producing metallocene catalyst under suitable polymerization conditions with propylene monomers and α,ω -diene monomers; and
recovering the propylene polymer.
15. The method of claim 14 wherein the metallocene catalyst is further defined as a zirconium metallocene catalyst.

16. The method of claim 14 wherein the contacting step includes hydrogen.
17. The method of claim 14 wherein the contacting step includes ethylene monomers.
18. A catalyst composition comprising:
 - (b) a high-melt-flow-rate-polymer-producing metallocene catalyst and
 - (c) a sufficient quantity of α,ω -diene monomerssuch that when the catalyst composition is contacted with a monomer under suitable polymerization conditions, the resulting polymer has
an MFR in the range of 0.1 to 19 g/10min; and
19. The catalyst composition of claim 18 wherein the metallocene catalyst is further defined as a zirconium metallocene catalyst.
20. The catalyst composition of claim 18 wherein the α,ω -diene is present in the range of 10 to 20,000 ppm.
21. The catalyst composition of claim 18 further including a mixture of meso and racemic metallocene catalysts.
22. A catalyst composition comprising:
a mixture of meso and racemic metallocene catalysts and
a quantity of α,ω -diene monomers.
23. A method of lowering MFR response of a high-melt-flow-rate-polymer-producing metallocene catalyst comprising contacting the metallocene catalyst with α,ω -diene monomer present in the range of 10 to 20,000 ppm,

such that when the catalyst composition is contacted with polymerizable reactants comprising propylene monomers under suitable polymerization conditions, the resulting polymer has

- an MFR in the range of 0.1 to 19 g/10min; and
- an 11% or greater increase in molecular weight distribution.

24. The method of claim 23 wherein the metallocene catalyst is further defined as a zirconium metallocene catalyst.
25. The method of claim 23 wherein the polymerization conditions further includes the presence of 100 to 50,000 ppm of hydrogen.
26. The method of claim 23, wherein the α,ω -diene is selected from the group consisting of 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, and 1,13-tetradecadiene.
27. The method of claim 23 wherein the α,ω -diene contains aliphatic, cyclic or aromatic substituents.
28. The method of claim 23 wherein the metallocene catalyst comprises one or more of:

Dimethylsilanylbis (2-methyl-4-phenyl-1-indenyl)ZrCl₂;

Dimethylsilanylbis(2-methyl-4,6-diisopropylindenyl)ZrCl₂;

Dimethylsilanylbis(2-ethyl-4-phenyl-1-indenyl)ZrCl₂;

Dimethylsilanylbis (2-ethyl-4-naphthyl-1-indenyl)ZrCl₂,

Phenyl(Methyl)silanylbis(2-methyl-4-phenyl-1-indenyl)ZrCl₂

Dimethylsilanylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2,4,6-trimethyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-ethyl-4-methyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2,4-dimethyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂, and
Dimethylsilanylbis(2-methyl-1-indenyl)ZrCl₂.

29. The method of claim 23 wherein the metallocene catalyst is contacted with an activator.
30. The method of claim 29 wherein the activator is an alkyl alumoxane.
31. The method of claim 30 wherein the alkyl alumoxane is methylalumoxane.
32. The method of claim 23 wherein the polymerization conditions are slurry polymerization conditions.
33. The method of claim 23 wherein the polymerizable reactants further comprise one or more of ethylene, C₂-C₁₀ α -olefins or diolefins.
34. The method of claim 23 wherein the polymerizable reactants further comprise ethylene, butene-1, pentene-1, hexene-1, heptene-1, 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 1-octene, 1-decene, 1-undecene, 1-dodecene, styrene or mixtures thereof.
35. The method of claim 23 wherein the metallocene catalyst is supported on a porous particulate material.

36. The method of claim 35 wherein the support comprises talc, inorganic oxides, inorganic chlorides, polyolefin compounds, or polymeric compounds.
37. The method of claim 35 wherein the support comprises a porous inorganic oxide metal oxides, where the metal is selected from Groups 2, 3, 4, 5, 13 or 14.
38. The method of claim 35 wherein the support comprises silica, alumina, silica-alumina, or mixtures thereof.
39. The method of claim 35 wherein the support comprises silicon dioxide.
40. The method of claim 35 wherein the support comprises one or more of talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide, thoria, aluminum phosphate gel, polyvinylchloride and substituted polystyrene.
41. A method of lowering MFR response of a high-melt-flow-rate-polymer-producing metallocene catalyst comprising contacting the metallocene catalyst with α,ω -diene monomer present in the range of 10 to 20,000 ppm, such that when the catalyst composition is contacted with polymerizable reactants comprising propylene monomers under suitable polymerization conditions, the resulting polymer has
 - an MFR in the range of 0.1 to 19 g/10min; and
 - an 11% or greater increase in molecular weight distribution; andwherein:
 - a) the α,ω -diene is selected from the group consisting of 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, and 1,13-tetradecadiene; and

b) the metallocene catalyst comprises one or more of:

Dimethylsilanylbis (2-methyl-4-phenyl-1-indenyl)ZrCl₂;
 Dimethylsilanylbis(2-methyl-4,6-diisopropylindenyl)ZrCl₂;
 Dimethylsilanylbis(2-ethyl-4-phenyl-1-indenyl)ZrCl₂;
 Dimethylsilanylbis (2-ethyl-4-naphthyl-1-indenyl)ZrCl₂,
 Phenyl(Methyl)silanylbis(2-methyl-4-phenyl-1-indenyl)ZrCl₂
 Dimethylsilanylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-methyl-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2,4,6-trimethyl-1-indenyl)ZrCl₂,
 Phenyl(Methyl)silanylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
 1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
 1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl₂,
 Phenyl(Methyl)silanylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-ethyl-4-methyl-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2,4-dimethyl-1-indenyl)ZrCl₂,
 Dimethylsilanylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂, and
 Dimethylsilanylbis(2-methyl-1-indenyl)ZrCl₂; and

c) the metallocene catalyst is contacted with an alkyl alumoxane; and

d) the polymerization conditions are slurry polymerization conditions; and

e) wherein the metallocene catalyst is supported on a porous inorganic oxide metal oxide of metals selected from Groups 2, 3, 4, 5, 13 or 14.

42. The method of claim 41 wherein the polymerizable reactants further comprise ethylene, butene-1, pentene-1, hexene-1, heptene-1, 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 1-octene, 1-decene, 1-undecene, 1-dodecene, styrene or mixtures thereof.

43. A method of lowering MFR response of a high-melt-flow-rate-polymer-producing metallocene catalyst comprising contacting the metallocene catalyst and an activator with α,ω -diene monomer present in the range of 10 to 20,000 ppm, such that when the catalyst composition is contacted with polymerizable reactants comprising propylene monomers under suitable polymerization conditions, the resulting polymer has

an MFR in the range of 0.1 to 19 g/10min; and

an 11% or greater increase in molecular weight distribution.
44. The method of claim 43 wherein the activator is modified methyl alumoxane.